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(54) **Drilling fluid additive for watersensitive shales and clays, and method of drilling using the same.**

(57) Disclosed is a drilling fluid additive for use with water sensitive shales, clays or fines, comprising a polymer, such as for example, polyvinylpyrrolidone, polyvinylalcohol, starches, cellulosic material, or partially hydrolyzed polyacrylamide, and comprising at least one of an alcohol such as a polypropylene glycol or an amphoteric surfactant such as a betaine. Also disclosed is an aqueous drilling fluid comprising such an additive, and a method of drilling water sensitive shales, clays or fines.

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According to even yet another embodiment of the present invention there is provided a method of stabilizing a subterranean formation penetrated by a borehole having water-sensitive materials. The method generally includes introducing a formation treatment fluid into the borehole and into contact with the formation, wherein the formation treatment fluid generally includes a cellulosic material, starches, polyvinylpyrrolidone or polyvinylalcohol, and a water soluble alcohol.

The well additive of the present invention generally includes a polymer and will further include a water soluble or near water soluble alcohol and/or an amphoteric surfactant. This well fluid additive finds utility in a broad range of well fluids in which it is desirable to stabilize water-sensitive shales, clays and other fines.

In the practice of the drilling method of the present invention, the drill string is rotated to cut a borehole into the earth while circulating a drilling fluid down through the drill string and thence up the annulus between the drilling string and the wall of the borehole. The drilling fluid utilized in the drilling method of the present invention will comprise an aqueous component and the additive of the present invention of polymer and a alcohol and/or a surfactant.

The aqueous medium employed in the well fluids of the present invention may be any kind of water from any source including, but not limited to, fresh water, sea water, water from the subterranean reservoir, sea water, or a natural or synthetic brine.

Polymers suitable to be utilized in the present invention will generally be water soluble. The polymers of the present invention preferably also have good wetting properties and a reasonable rate of dissolution in water for convenient use in the field. They should also afford particularly oil and gas wells. Additionally, it is preferable that the polymer be capable of encapsulating the water-sensitive shale, clay or other fines. It is also preferable that the polymer have suitable thermal stability for the environment in which they well fluids are employed. This generally means thermal stability up to and exceeding 2500F. It is also preferable that the polymer have suitable resistance to hydrolysis under high Ph, generally in the range of about 9 to about 11. Where necessary to achieve proper water solubility and other suitable properties, the polymers of the present invention may be hydrolyzed. For example, polyvinylpyrrolidone will generally be sixty percent or more hydrolyzed. Finally, it is also preferred that the polymers of the present invention have good tolerance to drilled solids contamination.

Examples of polymers suitable for use in the present invention include polyvinylpyrrolidone, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamides. Derivatized starches such as substituted and non-substituted alkyl starches, especially hydroxy propyl starches may be utilized as the polymer in the practice of the present invention.

The polyvinylpyrrolidone utilized in the present invention may be prepared by any suitable method known to those of skill in the art. The average molecular weight of the polyvinylpyrrolidone must be suitable for effective encapsulation of the drill cuttings and water sensitive shale, clay or fines. The higher end of the molecular weight range is generally dictated by solubility and viscosity limitations. Generally, the average molecular weight of the polyvinylpyrrolidone utilized in the present invention will be at least 10000, preferably in the range of about 10000 to about 1,500,000, more preferably in the range of about 500,000 to about 1,200,000, and most preferably in the range of about 750,000 to about 1,000,000.

The polyvinylalcohol of the present invention may be prepared by any suitable method known to those of skill in the art. The molecular weight of the polyvinylalcohol must be suitable for effective encapsulation of the drill cuttings and water sensitive shale, clay or fines. The higher end of the molecular weight range is generally dictated by solubility and viscosity limitations. Generally, the average molecular weight of the polyvinylalcohol utilized in the present invention will be at least 50,000, preferably in the range of about 50,000 to about 200,000, more preferably in the range of about 100,000 to about 175,000, and most preferably in the range of about 125,000 to about 175,000. Polyvinylalcohols suitable for use in the present invention will have a percent hydrolysis of at least 60 percent, and preferably in the range of about 80 to about 99 percent. Polyvinylalcohol may be utilized in solid or solution form.

The partially hydrolyzed polyacrylamides useful in the practice of the present invention may be obtained by any suitable method known to those of skill in the art. One suitable method generally involves polymerizing and subsequently hydrolyzing acrylamide (or a lower homolog of acrylamide) or copolymerizing acrylamide with an acrylate, or the like. The range of hydrolysis (and/or the proportion of the amide groups of the polyacrylamide that are carboxyl groups or have been hydrolyzed to form carboxyl groups) should be greater than about 20 percent. Preferably, the partially hydrolyzed polyacrylamide polymer will have a percent hydrolysis in the range of about 30 to about 50 percent. The molecular weight of the partially hydrolyzed polyacrylamide will be in the range of about 500,000 to about 20,000,000.

The term "partially hydrolyzed polyacrylamide" will generally include polyacrylamides as well as copolymers of acrylamide with other suitable monomers and polymers. Examples of other suitable polymers useful as partially hydrolyzed polyacrylamides includes partially hydrolyzed acrylamide/acrylate copolymers, partially hydrolyzed acrylamide/acrylic acid copolymers, and partially hydrolyzed acrylamide/styrene sulfonic acid

copolymers.

The alcohol soluble component of the well fluid additive of the present invention is generally selected from among water-soluble or poorly water insoluble alcohols and derivatives thereof. Such water-soluble or poorly water insoluble alcohols include mono-, di-, tri- and poly-hydric alcohols. Non-limiting examples of classes of alcohols suitable for use in the present invention include glycols, glycerols, sorbitols, and derivatives thereof.

Polyglycols suitable for use as the alcohol component of the present invention generally have a molecular weight that will render the polyglycol sufficiently water soluble or poorly water insoluble and of proper viscosity so as not to inhibit preparation and handling. Generally for most polypropyleneglycols, this means a molecular weight in the range of about 100 to about 1200. Accordingly, it is believed that for most polyglycols, a molecular weight above about 1200 will have a tendency to be water insoluble or at least not sufficiently water soluble for use in the present invention. Of course, in those instances where a certain polyglycol may have a molecular weight outside of the above range and still be suitable, it may certainly be utilized.

The alcohol component of the present invention may be a di-hydroxy alcohols, such as polyalkylene glycols, particularly polypropylene glycol. The alcohol component may also be a propoxylated tri-hydroxy alcohol such as polyalkylene glycerols, particularly polypropylene glycerol. Ethylene oxide propylene oxide copolymers of di-hydroxy and tri-hydroxy alcohols may also be utilized as the alcohol component.

Polypropylene glycols having a molecular weight in the range of about 200 to about 600 are most preferred for use as the alcohol component.

In the practice of the present invention when a water soluble component is utilized, the well fluid additive will generally comprise in the range of about 1 to about 99 volume percent water soluble component. Preferably, the well fluid additive will comprise in the range of about 5 to about 90 volume percent water soluble component. More preferably, the well fluid additive will comprise in the range of about 10 to about 80 volume percent, and most preferably in the range of about 30 to about 70 volume percent non-water soluble component.

The surfactant utilized in the practice of the present invention is selected from the class of surfactants known as betaines, which are themselves a special class of zwitterions. As a class, betaines are best known as foaming agents in products such as shampoos. Of course, foaming would be detrimental to drilling operations. Thus, it would be quite unexpected that a betaine would be suitable for use in a drilling fluid additive. Obviously, the betaines utilized in the present invention must not cause the well fluid to foam.

Suitable betaines can be selected by utilizing a simple foaming efficiency test.

The betaine utilized in the present invention may be mixed with the polymer, substituted onto the polymer, or copolymerized therein. Polymers made from betaine monomers and processes for their making are well known and are disclosed in US-A-4,742,135.

Preferred betaine polymers useful in the present invention include copolymers of acrylamide and vinylpyrrolidone with betaine. Such betaine polymers may be formed by a homogeneous, free radical, polymerization.

A particularly preferred betaine polymer is N-3 sulfopropyl-N-methacryloxyethyl-N, N-dimethyl ammonium betaine which is commercially available as SPE from Rachig Company of Germany. The polymeric betaine may be utilized in solid or liquid form.

Other commercially available suitable liquid based surfactants include Mirataine ASC, an alkylether hydroxypropyl sultaine from Rhone-Poulenc, and Mafo 13 from PPG.

The relative amounts of the components of the well fluid additive of the present invention are generally selected to provide compatibility with each other and with the well fluid, and to provide suitable shale, clay or fines stabilization.

Generally, based on the total weight of the well fluid additive, the well fluid additive of the present invention will comprise in the range of about 0.1 to about 50 weight percent polymer, in the range of about 0 to about 80 weight percent alcohol and in the range of about 0 to about 60 weight percent amphoteric surfactant. Preferably, the well fluid comprises in the range of about 5 to about 25 weight percent polymer, in the range of about 10 to about 70 weight percent alcohol and in the range of about 10 to about 40 weight percent amphoteric surfactant, and most preferably in the range of about 10 to about 20 weight percent polymer, in the range of about 20 to about 50 weight percent alcohol and in the range of about 20 to about 30 weight percent amphoteric surfactant.

In the practice of the present invention, the well fluid additive is generally added to the well fluid in an amount in the range of about 3.5 to about 70 pounds/bbl well fluid.

It is also to be understood that other additives used by those of skill in the art may also be added to the drilling fluids of the present invention, as long as they do not have a substantial detrimental effect on the well fluid, including but not limited to for example, surfactants, weighting materials, breakers, loss circulation additives and salts.

Baker Hughes Inteq.

The samples were stirred for 45 minutes. The samples were then rolled for four hours at 1500F after which time 25g of HOLE-PLUG was added to each sample. Next the samples were rolled for 16 hours at 2500F and then sieved on an 18-mesh screen. The remaining HOLE-PLUG was washed, dried for four hours at 2500F, and weighed. Percent erosion was calculated, assuming an initially determined moisture content of 8.8%.

The results are presented in TABLE 5 wherein the "A" series of samples is without betaine, and the "B." series is with betaine. Numbers 1 are with PVP, numbers 2 are with PVA, numbers 3 are with PHPA, and numbers 4 are without polymer. The drilling fluid samples are identical except for varying the type of polymer and the presence of absence of betaine.

The presence of betaine improved the percentage of erosion loss for PVA, PHPA and the seawater. The erosion loss for PVP remained unchanged.

The presence of betaine improved the API fluid loss data for PVP, PVA and seawater without polymer, with the API fluid loss data for PHPA not changing.

The stability of the yield point data and the 10-min gel data was very similar with or without betaine.

#### Example 6: Betaine With Various Polymers - Freshwater Base

Drilling fluids were formulated as shown in TABLE 6 using freshwater with PVP, PVA, or partially hydrolyzed polyacrylamide polymer ("PHPA"), both with and without betaine.

TABLE 5 Comparison of Polymers in Seawater Base - Rolling Erosion Study

<b>MATERIALS</b>									
	A-1	A-2	A-3	A-4	B-1	B-2	B-3	B-4	
Seawater, bbl	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	
Luviskol K-90, lb	2.0				2.0				
MTM PVA, lb		2.0				2.0			
NEW-DRILL PLUS, lb			2.0				2.0		
Caustic soda, bbl	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
MIL-PAC LV, lb	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	
Biozan, lb	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	
Mirataine ASC, lb					7.0	7.0	7.0	7.0	
MIL-BAR, lb	204	204	204	204	204	204	204	204	
<b>PROPERTIES</b>									
Apparent Viscosity, cp	33	24.5	39	27.5	35.5	32	34	34	
Plastic Viscosity, cp	22	16	26	16	25	20	23	22	
Yield Point, lb/100 sqft.	22	17	26	23	21	24	22	24	
10-sec Gel, lb/100 sqft.	5	3	5	6	4	5	5	8	
10-min Gel, lb/100 sqft	7	4	7	7	6	7	6	11	
API Fluid Loss, ml	7.8	10.6	3.4	96	5.4	5.8	3.4	18	
HOLE-PLUG, g (after wash and dry)	20.7	18.2	11.2	7.9	20.7	18.6	19.7	14.6	
% Erosion Loss	9.2	20.2	50.9	65.4	9.2	18.4	13.6	36.0	

The base fluid was freshwater.

The PVP utilized in this example was Luviskol K-90 from BASF. The PVA utilized in this example is avail-

able from MTM Research Chemicals, and the PHPA utilized is NEW DRILL PLUS (Trade Mark), available from Baker Hughes Inteq.

The samples were stirred for 45 minutes. The samples were then rolled for four hours at 150 degrees F, after which time the samples were rolled for 16 hours at 250 degrees F and then sieved on an 18-mesh screen. The remaining HOLE-PLUG was washed, dried for four hours at 250 degrees F, and weighed. Percent erosion was calculated, assuming an initially determined moisture content of 8.8%.

The results are presented in TABLE 6 wherein the "A" series of samples is without betaine, and the "B" series is with betaine. Numbers 1 are freshwater with PVP, numbers 2 are with PVA, and numbers 3 are with PHPA. The drilling fluid samples are identical except for varying the type of polymer and the presence of absence of betaine.

In the presence of betaine, PHPA showed an improvement in erosion loss data, yield point data, and 10-min gel data.

#### Example 7: Comparison of Polymers in Freshwater With Inhibitive Salts

Drilling fluids were formulated as shown in TABLE 7 using freshwater with PVP, PVA, or partially hydrolyzed polyacrylamide polymer ("PHPA"), both with and without betaine. Potassium carbonate and gypsum were added as inhibitive salts.

The samples were stirred for 45 minutes. Next, 25g of HOLE-PLUG was added to the samples, which were then rolled for 16 hours at 250 degrees F, and then sieved on an 18- mesh screen. The

TABLE 6 Comparison of Polymers with Freshwater Base - Rolling Erosion Study

<b>MATERIALS</b>						
	A-1	A-2	A-3	B-1	B-2	B-3
Freshwater, bbl	0.86	0.86	0.86	0.86	0.86	0.86
Luviskol K-90, lb	1.0			1.0		
MTM PVA, lb		1.0			1.0	
NEW-DRILL PLUS, lb			1.0			1.0
Caustic soda, bbl	0.1	0.1	0.1	0.1	0.1	0.1
MIL-PAC LV, lb	1.0	1.0	1.0	1.0	1.0	1.0
Biozan, lb	0.3	0.3	0.3	0.3	0.3	0.3
Mirataine ASC, lb				7.0	7.0	7.0
MIL-BAR, lb	204	204	204	204	204	204
<b>PROPERTIES</b>						
Apparent Viscosity, cp	86	92	50	94	85.5	48.5
Plastic Viscosity, cp	58	59	44	63	54	41
Yield Point, lb/100 sqft.	56	66	12	62	63	15
10-sec Gel, lb/100 sqft.	17	25	3	22	19	3
10-min Gel, lb/100 sqft	30	36	6	34	28	7
API Fluid Loss, ml	10.2	10.6	6.5	10.6	14.4	6.6
HOLE-PLUG, g (after wash and dry)	1.6	1.4	0.6	0.2	2.3	12.6
% Erosion Loss	93.0	93.9	97.4	99.1	90	44.7

remaining HOLE-PLUG was washed, dried for four hours at 250 degrees F, and weighed. Percent erosion was calculated, assuming an initially determined moisture content of 8.8%. The results are presented in TABLE 7. The "A" series of samples contain potassium carbonate as the inhibitive salt. The "B" series of samples contain gypsum as the inhibitive salt. Sample numbers 1 contain PVP, sample numbers 2 contain PVA, and sample numbers 3 contain PHPA.

Example 8: Evaluation of Glycol in PVP1 PVA and PHPA Seawater System

Drilling fluids were formulated as shown in TABLE 8 using seawater with PVP, PVA, or partially hydrolyzed polyacrylamide polymer ("PHPA"), using none, one or both of betaine and glycol.

The PVP utilized was K-90 from BASF. The PVA utilized was Airvol 540S from Air Products, and the PHPA was NEW-DRILL PLUS available from Baker Hughes Inteq. The betaine used was Mirataine ASC from Rhone-Poulenc. The glycol was Glycol No. 3192 available from Baker Performance Chemicals.

The samples were stirred for 45 minutes. Next, 25g of HOLE-PLUG was added to the samples, which were then rolled for 16 hours at 250 degrees F, and then sieved on an 18-mesh screen. The remaining HOLE-PLUG was washed, dried for four hours at 250 degrees F, and weighed. Percent erosion was calculated, assuming an initially determined moisture content of 8.8%. The results are presented in TABLE 8. The "A" series of samples have neither betaine nor glycol. The "B" series of samples contain betaine. The "C" series of samples contain both betaine and glycol. Finally, the "D" series of samples contain glycol.

Sample numbers 1 contain PVP, sample numbers 2 contain PVA, old

TABLE 7 Comparison of Polymers in Freshwater Base With Inhibitive Salts

MATERIALS	A-1	A-2	A-3	B-1	B-2	B-3
Freshwater, bbl	0.86	0.86	0.86	0.86	0.86	0.86
PVP K-90, lb	0.6			0.6		
PVA Airvol 540S, lb		0.6			0.6	
NEW-DRILL PLUS, lb			0.6			0.6
Caustic soda, bbl	0.1	0.1	0.1	0.1	0.1	0.1
Potassium carbonate, lb	10	10	10			
Gypsum, lb				6.0	6.0	6.0
MIL-PAC LV, lb	1.0	1.0	1.0	2.0	2.0	2.0
Biozan, lb	0.5	0.5	0.5	0.5	0.5	0.5
Miramine ASC, lb				7.0	7.0	7.0
MIL-BAR, lb	204	204	204	204	204	204
PROPERTIES						
Apparent Viscosity, cp	8.5	13.5	12.5	48	44	48.5
Plastic Viscosity, cp	8	10	10	31	28	33
Yield Point, lb/100 sqft.	1	7	5	34	32	31
10-sec Gel, lb/100 sqft.	1	2	1	8	7	7
10-min Gel, lb/100 sqft	1	4	1	10	10	10
API Fluid Loss, ml	15.8	14	9.9	10.8	11.7	13.6
HOLE-PLUG, g (after wash and dry)	17.1	17.3	14.2	6.0	5.9	6.0
% Erosion Loss	25.0	24.1	37.7	73.7	74.1	73.7

TABLE 8 Glycol No. 3192 In Various Polymer Seawater Systems

MATERIALS	A-1	A-2	A-3	A-4	B-1	B-2	B-3	B-4	C-1	C-2	C-3	D-1	D-2	D-3
Seawater, bbl	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86
Caustic Soda, lb	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PVP K-90, lb	2.0				2.0				2.0			2.0		
PVA Airvol 540S, lb		2.0				2.0				2.0			2.0	
NEW-DRILL PLUS, lb			2.0				2.0				2.0			2.0
MIL-PAC LV, lb	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Biozan, lb	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Mirataine ASC, lb					7.0	7.0	7.0	7.0	7.0	7.0	7.0			
Glycol No. 3192, lb									17.5	17.5	17.5	17.5	17.5	17.5
MIL-BAR, lb	204	204	204	204	204	204	204	204	204	204	204	204	204	204
PROPERTIES														
Apparent Viscosity, cp	33	24.5	39	27.5	35.5	32	34	34	35	32	49.5	47.5	44.5	60
Plastic Viscosity, cp	22	16	26	16	25	20	23	22	22	20	30	35	33	37
Yield Point, lb/100 sqft.	22	17	26	23	21	24	22	24	26	24	39	25	23	45
API FLUID LOSS, ml	7.8	10.6	3.4	96	5.4	5.8	3.4	18	2.4	3.6	5.0	5.6	6.0	2.4
%Erosion Loss (calc on initial 8.8% moisture)	9	20	51	65	9	18	14	36	0	11	22	0	0	37

sample numbers 3 contain PHPA, and samples number 4 are seawater without polymer.

In determining the effect of betaine only, comparison of the "A" series with the "B" series shows that erosion loss data is improved for PVA and PHPA and seawater, and PVP remains unchanged. The API fluid loss data shows improvement for PVP, PVA, seawater, and no change for PHPA. In determining the effect of glycol only, the "A" series is compared with the "D" series. Both the erosion loss data and the API Fluid Loss data show improvement for PVP, PVA and PHPA.

To determine the effect of the combination of betaine and glycol, over drilling fluids having neither, the "A" series is compared to the "C" series. The erosion loss data shows improvement for PVP, PVA and PHPA. The API Fluid Loss data shows improvement for PVP and PVA. To determine the existence of a "synergistic" effect of using both glycol and betaine, the "B", "C" and "D" series are all examined together.

For the API fluid loss data for PVP, betaine yields 5.4 ml/30min/100psi and PVP yields 5.6 ml/30min/100psi. Surprisingly, the combination yields 2.4 ml/30min/100psi which combination is better than each separately.

A similar observation is made for the API fluid loss data for PVA. With betaine, the PVA API fluid loss is 5.8ml/30min/100psi, and with glycol, the PVA API fluid loss is 6.0. Again, surprisingly, the combination yields 3.6.

#### Example 9: Evaluation of Glycol 3192 With Various Polymers in 10% KCl and 20% NaCl

Drilling fluids were formulated as shown in TABLE 9A and TABLE 9B using 10% Kcl water and 20% NaCl water, respectively, with PVP, PVA, or partially hydrolyzed polyacrylamide polymer

TABLE 9-A Glycol No. 3192 In Various Polymer Systems With 10%KCL WATER

<b>MATERIALS</b>									
	A-1	A-2	A-3	B-1	B-2	B-3	C-1	C-2	C-3
10% KCl water, bbl	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86
Caustic Soda, lb	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PVP K-90, lb	2.0			2.0			2.0		
PVA Airvol 540S, lb		2.0			2.0			2.0	
NEW-DRILL PLUS, lb			2.0			2.0			2.0
MIL-PAC LV, lb	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Biozan, lb	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Mirataine ASC, lb							7.0	7.0	7.0
Glycol No. 3192, lb				17.5	17.5	17.5			
MIL-BAR, lb	204	204	204	204	204	204	204	204	204
<b>PROPERTIES</b>									
Apparent Viscosity, cp	18.5	33.5	28	25.5	41.5	30	27	36	49.5
Plastic Viscosity, cp	16	22	21	29	24	26	22	24	34
Yield Point, lb/100 sqft.	5	23	14	22	35	8	10	24	31
API FLUID LOSS, ml	7.8	4.0	7.6	4.0	3.2	2.0	6.2	4.4	4.0
%Erosion Loss (calc on initial 8.8% moisture)	13	9	25	4	4	19	6	3	4

TABLE 9-B Glycol No. 3192 In Various Polymer Systems With 20% NaCl WATER

MATERIALS	A-1	A-2	A-3	B-1	B-2	B-3	C-1	C-2	C-3
20% NaCl water, bbl	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86
Caustic Soda, lb	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PVP K-90, lb	2.0			2.0			2.0		
PVA Airvol 540S, lb		2.0			2.0			2.0	
NEW-DRILL PLUS, lb			2.0			2.0			2.0
MIL-PAC LV, lb	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Biozan, lb	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Mirataine ASC, lb							7.0	7.0	7.0
Glycol No. 3192, lb				17.5	17.5	17.5			
MIL-BAR, lb	204	204	204	204	204	204	204	204	204
PROPERTIES									
Apparent Viscosity, cp	21.5	20.5	30	25.5	29.5	33.5	18	24.5	58.5
Plastic Viscosity, cp	21	14	26	22	22	30	16	18	43
Yield Point, lb/100 sqft.	1	13	8	7	15	7	4	13	31
API FLUID LOSS, ml	7.6	9.4	4.0	4.6	8.6	21	4.8	10.8	3.6
% Erosion Loss (calc on initial 8.8% moisture)	28	19	41	3	12	26	13	8	8

("PHPA"), using none or one of the betaine and the glycol.

The PVP utilized was K-90 from BASF. The PVA utilized was Airvol 540S from Air Products, and the PHPA was NEW-DRILL PLUS available from Baker Hughes Inteq. The betaine used was Mirataine ASC from Rhone-Poulenc. The glycol was Glycol No. 3192 available from Baker Performance Chemicals.

The samples were stirred for 45 minutes. Next, 25g of HOLE-PLUG was added to the samples, which were then rolled for 16 hours at 250 degrees F, and then sieved on an 18-mesh screen. The remaining HOLE-PLUG was washed, dried for four hours at 250 degrees F, and weighed. Percent erosion was calculated, assuming an initially determined moisture content of 8.8%. The results are presented in TABLES 9A and 9B.

PVA appears to have some problems in the presence of higher concentrations of monovalent salts. The "A" series of samples have neither betaine nor glycol. The "B" series of samples contain glycol, and the "C" series of samples contain betaine

Sample numbers 1 contain PVP, sample numbers 2 contain PVA, and sample numbers 3 contain PHPA.

Referring now to TABLE 9A, the presence of either betaine or glycol improves the erosion loss data for PVP, PVA and PHPA. The presence of glycol improves the API Fluid Loss data for PVP, PVA and PHPA. The

presence of betaine improves the API Fluid Loss data for PVP and PHPA.

Referring now to TABLE 9B, the presence betaine improves the erosion loss data for PVP, PVA and PHPA. The presence of glycol improves the erosion loss data for PVP and PVA. The presence of betaine improves the API Fluid Loss data for PVP and PHPA. The presence of glycol improves the API Fluid Loss data for PVP and PVA.

#### Example 10: Glycol No. 3274 In Various Polymer And Water Systems

Drilling fluids were formulated as shown in TABLE 10 using seawater, 10% KCl water and 20% NaCl water, with PVP, PVA, or partially hydrolyzed polyacrylamide polymer ("PHPA"), with or without the glycol (only sample A-3 contained betaine).

The PVP utilized was K-90 from BASF. The PVA utilized was Airvol 540S from Air Products, and the PHPA was NEW-DRILL PLUS available from Baker Hughes Inteq. The betaine used was Mirataine ASC from Rhone-Poulenc. The glycol was Glycol No. 3274 available from Baker Performance Chemicals.

The samples were stirred for 45 minutes. Next, 25g of HOLE-PLUG was added to the samples, which were then rolled for 16 hours, at 250 degrees F, and then sieved on an 18-mesh screen. The remaining HOLE-PLUG was washed, dried for four hours at 250 degrees F, and weighed. Percent erosion was calculated, assuming an initially determined moisture content of 8.8%. The results are presented in TABLE 10. Series "A" samples contain seawater, series "B" samples contain 10% KCl water, and series "C" samples contain 20% NaCl water. For series "B" and "C", numbers 1-3 have no glycol and numbers 4-6 have glycol. Also for series "B" and "C", numbers 1 and 4 are PVP, numbers 2 and 5 are PVA, and numbers 3 are PHPA.

#### Example 11.

Drilling fluids were formulated as shown in TABLE 11 using seawater only and with PVP, PVA, or partially hydrolyzed polyacrylamide polymer ("PHPA"), using none or either the glycol or both the betaine and the glycol. The PVP utilized was K-90 from BASF. The PVA utilized was Airvol 540S from Air Products, and the PHPA was NEW-DRILL PLUS available from Baker Hughes Inteq. The betaine used was Mirataine ASC

TABLE 10 Glycol No. 3274 In Various Polymer And Various Water Systems

MATERIALS	A-1	A-2	A-3	A-4	A-5	B-1	B-2	B-3	B-4	B-5	B-6	C-1	C-2	C-3	C-4	C-5	C-6
Seawater, bbl	0.86	0.86	0.86	0.86	0.86												
10% KCl Water, bbl						0.86	0.86	0.86	0.86	0.86	0.86						
20% NaCl Water, bbl												0.86	0.86	0.86	0.86	0.86	0.86
Caustic Soda, lb	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PVP K-90, lb						2.0			2.0			2.0			2.0		
PVA Airvol 540S, lb							2.0			2.0			2.0			2.0	
NEW-DRILL PLUS, lb			2.0					2.0			2.0			2.0			2.0
MIL-PAC LV, lb	2.0	2.0	2.0					2.0			2.0			2.0			2.0
Biozan, lb	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Mirastine ASC, lb			7.0														
Glycol No. 3274, lb		17.5	17.5		17.5				17.5	17.5	17.5				17.5	17.5	17.5
MIL-BAR, lb	204	204	204	204	204	204	204	204	204	204	204	204	204	204	204	204	204
PROPERTIES																	
Apparent Viscosity, cp	39	27.5	35	27.5	30	18.5	33.5	28	21	37.5	18	25.5	29.5	33.5	34.5	31.5	13.5
Plastic Viscosity, cp	26	19	25	16	18	16	22	21	15	25	16	22	22	30	29	23	13
Yield Point, lb/100 sqft.	26	17	20	23	24	5	23	14	6	25	4	7	15	7	11	17	1
API FLUID LOSS, ml	3.4	N/C	18.8	96	10.4	7.8	4.0	7.6	4.0	2.0	4.4	4.6	8.6	21	2.4	5.0	20
% Erosion Loss (calc on initial 8.8% moisture)	51	21	10	65	18	13	9	25	8	3	8	3	12	26	10	0	20

from Rhone-Poulenc. The glycol was Aquacol D available from Baker Performance Chemicals.

The samples were stirred for 45 minutes. Next, 25g of HOLE-PLUG was added to the samples, which were then rolled for 16 hours at 250 degrees F, and then sieved on an 18-mesh screen. The remaining HOLE-PLUG was washed, dried for four hours at 250 degrees F, and weighed. Percent erosion was calculated, assuming an initially determined moisture content of 8.8%. The results are presented in TABLE 11.

In TABLE 11, sample series "A" contains PVP, series "B" contains "PVA", series "C" contains PHPA, and series "D" is seawater without polymer. Numbers 1 have neither betaine nor glycol, numbers 2 have glycol, and numbers 3 have both betaine and glycol.

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TABLE 11 GLYCOL "AQUACOL D" In Various Polymer Seawater Systems

MATERIALS	A-1	A-2	A-3	B-1	B-2	B-3	C-1	C-2	C-3	D-2	D-3
Seawater, bbl	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86	0.86
Caustic Soda, lb	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PVP K-90, lb	2.0	2.0	2.0								
PVA Airvol 540S, lb				2.0	2.0	2.0					
NEW-DRILL PLUS, lb							2.0	2.0	2.0		
MIL-PAC LV, lb	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Biozan, lb	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Mirataine ASC, lb			7.0			7.0			7.0		7.0
Aquacol D, lb		17.5	17.5		17.5	17.5		17.5	17.5	17.5	17.5
MIL-BAR, lb	204	204	204	204	204	204	204	204	204	204	204
PROPERTIES											
Apparent Viscosity, cp	33	50	42	24.5	44.5	42	39	62	57.5	27.5	32.5
Plastic Viscosity, cp	22	34	30	16	33	32	26	37	35	16	21
Yield Point, lb/100 sqft.	22	32	24	17	23	20	26	52	45	23	23
API FLUID LOSS, ml	7.8	5.6	6.0	10.6	5.6	6.0	3.4	1.6	2.4	96	6.4
%Erosion Loss (calc on initial 8.8 % moisture)	9	0	9	20	25	16	51	36	32	65	59

**Claims**

1. A well fluid additive comprising:
  - (a) at least one polymer selected from the group of polymers consisting of polymeric cellulose, derivatized starches, polyvinylpyrrolidone polyvinylalcohol and partially hydrolyzed polyacrylamide; and
  - (b) a non-foaming amphoteric surfactant or a water soluble alcohol.
2. The well fluid additive of claim 1 wherein the amphoteric surfactant is a betaine.
3. The well fluid additive of claim 2 wherein the betaine is incorporated into the polymer.
4. The well fluid additive of any one of claims 1 to 3 wherein the additive comprises in the range of about 0.1 to about 50 weight percent polymer, in the range of about 0 to about 60 weight percent alcohol and in the range of about 0 to about 60 weight percent amphoteric surfactant.
5. The well fluid additive of any one of claim 1 to 4 wherein the water soluble alcohol is selected from among glycols, glycerols, sorbitors and derivatives thereof.
6. The well fluid additive of any one of claims 1 to 5 wherein the alcohol is a polyglycol having a molecular weight in the range of about 100 to about 1200.
7. The well fluid additive of any one of claims 1 to 5 wherein the alcohol is a polypropylene glycol having a molecular weight in the range of about 200 to about 600, the amphoteric surfactant is a betaine.
8. The well fluid additive of any one of claims 1 to 7 wherein the alcohol is a polypropylene glycol.
9. The well fluid additive of any one of claims 1 to 8 comprising both an amphoteric surfactant and a water soluble alcohol.
10. A well fluid comprising an aqueous component and the well fluid of any one of claims 1 to 9.
11. A method of stabilizing a subterranean formation penetrated by a borehole and wherein the formation comprises water-sensitive materials, the method comprising introducing a formation treatment fluid into the borehole and into contact with the formation, wherein the formation treatment fluid comprises the well fluid additive of any one of claims 1 to 9.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 95 30 0980

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	GB-A-2 086 923 (NL INDUSTRIES INC.) * page 2, line 21 - page 3, line 39 * * examples 1-11 * ---	1,4-8, 10,11	C09K7/00 C09K7/02
X,D	US-A-5 076 373 (A.H.HALE) * column 2, line 40 - column 3, line 56 * * claims 1-4 * ---	1,4-6, 10,11 7,8	
Y	US-A-5 260 269 (A.H.HALE) * column 2, line 65 - column 3, line 20 * * column 3, line 62 - column 4, line 35 * ---	1,4-8, 10,11	
Y	FR-A-2 624 132 (BAKER HUGHES) * page 6, line 3 - line 31 * * page 7, line 4 - line 18 * ---	1,4-8, 10,11	
Y	WO-A-94 02567 (K.B.TECHNOLOGIES) * page 21, line 4 - page 22, line 14 * * page 23, line 15 - line 23 * * claims 1,8-13,22,28 * ---	1,10,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6)  C09K
Y	EP-A-0 037 996 (ZH.GOLDSCHMIDT) * page 4, line 6 - line 28 * ---	1-4,10, 11	
Y	PATENT ABSTRACTS OF JAPAN vol. 016 no. 387 (C-975), 18 August 1992 & JP-A-04 126788 (SEKIYU KOUDAN) 27 April 1992, * abstract * -----	1-4,10, 11	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>19 May 1995</b>	Examiner <b>Boulon, A</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- A : member of the same patent family, corresponding document	

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